

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE



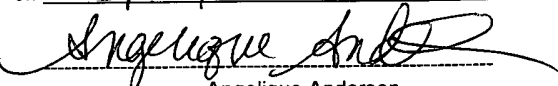
International Application of:
Stamires, D., et al.
Serial No.: 10/071,386
Filing Date: February 7, 2002

: Docket: ACH2852US
:
: Examiner:
:
: Group Art Unit: 1754

For: PROCESS FOR THE PREPARATION OF
ANIONIC CLAY AND BOEHMITE-CONTAINING
COMPOSITIONS

Commissioner of Patents and Trademarks
Washington, D.C. 20231

CERTIFICATE OF MAILING
I hereby certify that this correspondence is being
deposited with the United States Postal Service as
First-Class mail in an envelope addressed to:
Assistant Commissioner for Patents
Washington, DC 20231

on 3/15/02


Angelique Anderson

SUBMISSION OF CERTIFIED COPY OF PRIORITY DOCUMENT

Sir:

Enclosed herewith is a certified copy of European Patent Application No.
01200805.8, dated March 3, 2001 in connection with the above-identified application.

Respectfully submitted,


Louis A. Morris
Attorney for Applicants
Reg. No. 28,100

Akzo Nobel Inc.
Intellectual Property Dept.
7 Livingstone Avenue
Dobbs Ferry, New York 10522
(312) 906-7769



Europäisches
Patentamt

European
Patent Office

Office européen
des brevets



Bescheinigung

Certificate

Attestation

Die angehefteten Unterla-
gen stimmen mit der
ursprünglich eingereichten
Fassung der auf dem näch-
sten Blatt bezeichneten
europäischen Patentanmel-
dung überein.

The attached documents
are exact copies of the
European patent application
described on the following
page, as originally filed.

Les documents fixés à
cette attestation sont
conformes à la version
initialement déposée de
la demande de brevet
européen spécifiée à la
page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

01200805.8

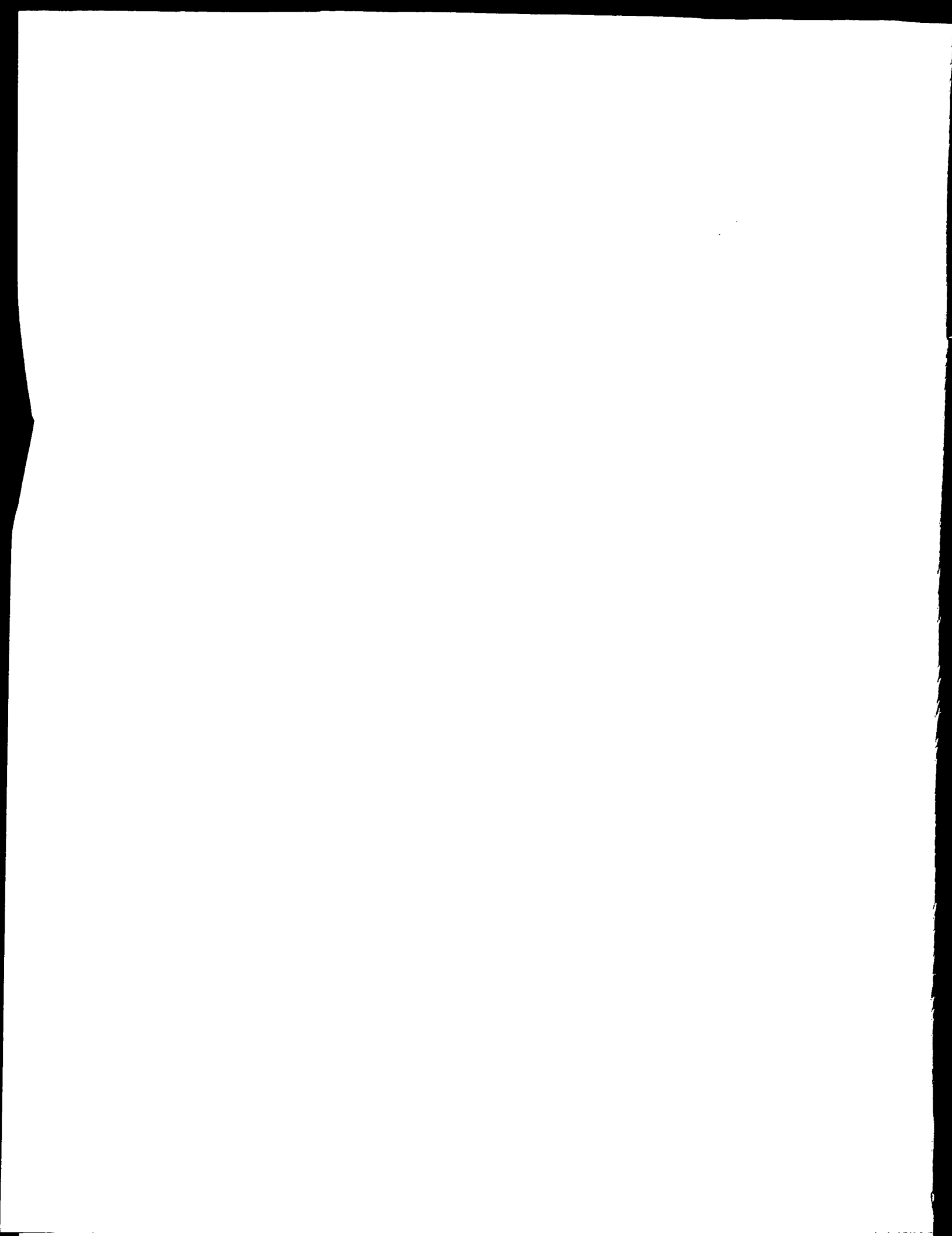
Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk

DEN HAAG, DEN
THE HAGUE, 08/02/02
LA HAYE, LE





Europäisches
Patentamt

European
Patent Office

Office européen
des brevets

Blatt 2 der Bescheinigung
Sheet 2 of the certificate
Page 2 de l'attestation

Anmeldung Nr.:
Application no.:
Demande n°:

01200805.8

Anmeldetag:
Date of filing:
Date de dépôt:

05/03/01

Anmelder:
Applicant(s):
Demandeur(s):
Akzo Nobel N.V.
6824 BM Arnhem
NETHERLANDS

Bezeichnung der Erfindung:
Title of the invention:
Titre de l'invention:

Process for the preparation of anionic clay and boehmite-containing compositions

In Anspruch genommene Priorität(en) / Priority(ies) claimed / Priorité(s) revendiquée(s)

Staat: US
State:
Pays:

Tag: 09/02/01
Date:
Date:

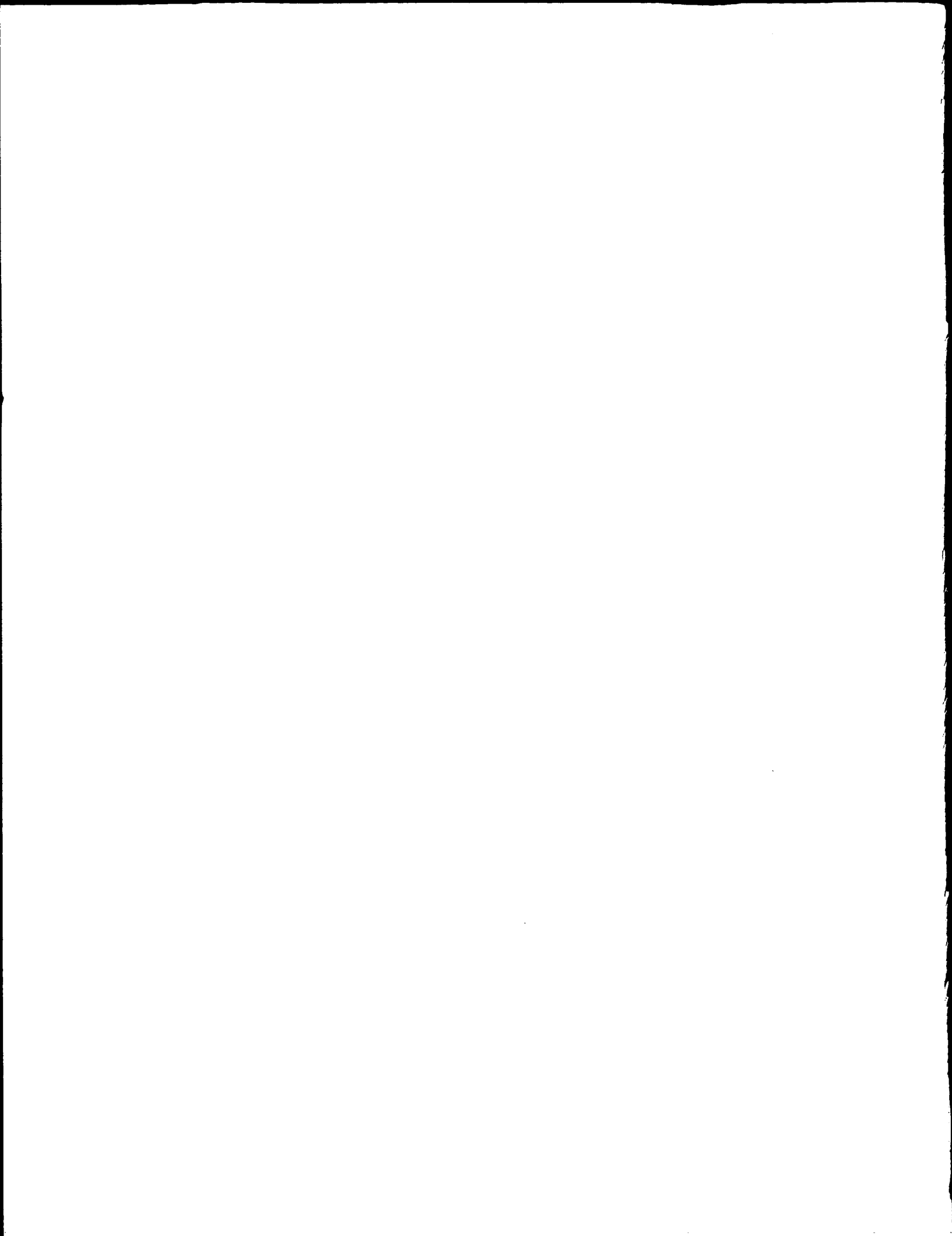
Aktenzeichen: USA 103678
File no.
Numéro de dépôt:

Internationale Patentklassifikation:
International Patent classification:
Classification internationale des brevets:

/

Am Anmeldetag benannte Vertragsstaaten:
Contracting states designated at date of filing: AT/BE/CH/CY/DE/DK/ES/FI/FR/GB/GR/IE/IT/LI/LU/MC/NL/PT/SE/TR
Etats contractants désignés lors du dépôt:

Bemerkungen:
Remarks:
Remarques:



EPO - DG 1

05. 03. 2001

(38)

ACH 2852 PDEP

PROCESS FOR THE PREPARATION OF ANIONIC CLAY AND BOEHMITE-CONTAINING COMPOSITIONS

BACKGROUND OF THE INVENTION

5

This invention relates to a process for the preparation anionic clay and boehmite-containing compositions. The invention also relates to the preparation of catalyst compositions comprising anionic clay and boehmite-containing compositions.

10

Anionic clays have a crystal structure which consists of positively charged layers built up of specific combinations of metal hydroxides between which there are anions and water molecules. Hydrotalcite is an example of a naturally occurring anionic clay, in which carbonate is the predominant anion present.

15

Meixnerite is an anionic clay wherein hydroxyl is the predominant anion present.

20

In hydrotalcite-like anionic clays the brucite-like main layers are built up of octahedra alternating with interlayers in which water molecules and anions, more particularly carbonate ions, are distributed. The interlayers may contain anions such as NO_3^- , OH , Cl^- , Br^- , I^- , SO_4^{2-} , SiO_3^{2-} , CrO_4^{2-} , BO_3^{2-} , MnO_4^- , HGaO_3^{2-} , HVO_4^{2-} , ClO_4^- , BO_3^{2-} , pillaring anions such as $\text{V}_{10}\text{O}_{28}^{6-}$ and $\text{Mo}_7\text{O}_{24}^{6-}$, monocarboxylates such as acetate, dicarboxylates such as oxalate, alkyl sulphonates such as laurylsulphonate.

25

It should be noted that a variety of terms are used to describe the material that is referred to in this specification as an anionic clay. Hydrotalcite-like and layered double hydroxide are interchangeably used by those skilled in the art.

In this specification we refer to these materials as anionic clays, comprising within that term hydrotalcite-like and layered double hydroxide materials.

30

These anionic clays can contain different divalent or trivalent metals. The most commonly described anionic clays are Mg-Al anionic clays. In the prior art the emphasis is usually on this type of anionic clays, whereas anionic clays containing other divalent and/or trivalent metals are only mentioned in passing, even though the chemistry of their preparation and their properties can be very different and unpredictable. Mg-Al anionic clays are suitable for many applications in the absorbent and catalysts field. Anionic clays from other divalent and/or trivalent metal have specific applications in these fields. Fe-Al anionic clays, for instance, are useful as hydrogenation catalysts; Zn-Cr anionic clays can be used as catalysts in oxidation reactions.

Anionic clays have been described in many prior art publications. Two major reviews of anionic clay chemistry were published in which the synthesis methods available for anionic clay synthesis have been summarised:

F. Cavani et al "Hydrotalcite-type anionic clays: Preparation, Properties and Applications," Catalysis Today, 11 (1991) Elsevier Science Publishers B. V. Amsterdam.

J P Besse and others "Anionic clays: trends in pillary chemistry, its synthesis and microporous solids"(1992), 2, 108, editors: M.I. Occelli, H.E. Robson, Van Nostrand Reinhold, N.Y.

In these reviews basically two types of anionic clay preparation are described. The most conventional method is co-precipitation (in Besse this method is called the salt-base method) of a soluble divalent metal salt and a soluble trivalent metal salt, optionally followed by hydrothermal treatment or aging to increase the crystallite size. The second method is the salt-oxide method in which a divalent metal oxide is reacted at atmospheric pressure with a soluble trivalent metal salt, followed by aging under atmospheric pressure. This method has only been described for the use of ZnO and CuO in combination with soluble trivalent metal salts.

30

For work on anionic clays, reference is further made to the following articles:

Helv. Chim. Acta, 25, 106-137 and 555-569 (1942)

J. Am. Ceram. Soc., 42, no. 3, 121 (1959)

Chemistry Letters (Japan), 843 (1973)

Clays and Clay Minerals, 23, 369 (1975)

5 Clays and Clay Minerals, 28, 50 (1980)

Clays and Clay Minerals, 34, 507 (1996)

Materials Chemistry and Physics, 14, 569 (1986).

In addition there is an extensive amount of patent literature on the use of anionic clays and processes for their preparation.

10

Recently, patent applications relating to the production of anionic clays from inexpensive raw materials have been published. These materials include magnesium oxide, aluminium trihydrate and boehmite.

15 WO 99/41198 relates to the production of anionic clay from two types of aluminium compounds and a magnesium source. One of the aluminium sources is aluminium trihydrate or a thermally treated form thereof.

20 WO 99/41196 discloses the preparation of anionic clays with acetate as the charge balancing anion from magnesium acetate, another magnesium source and aluminium trihydrate.

In WO 99/41195 a continuous process is described for the production of a Mg-Al anionic clay from a Mg source and aluminium trihydrate.

25 WO 99/41197 discloses the production of an anionic clay-containing composition comprising a Mg-Al anionic clay and unreacted aluminium trihydrate.

30 WO 00/44672 discloses the production of anionic clays by hydrothermal treatment of a slurry of a magnesium source and boehmite, which has been peptised by an inorganic acid. By using an excess of boehmite, unreacted

boehmite ends up in the composition.

WO 00/44671 relates to compositions comprising Mg-Al anionic clay and boehmite. These compositions are prepared from boehmite and a magnesium source not being hydromagnesite. The boehmite in the composition results from
5 an excess of boehmite starting material, which ends up in the composition as unreacted boehmite.

There are many applications of anionic clays. These include but are not
10 restricted to: catalysts, adsorbents, drilling muds, catalyst supports and carriers, extenders and applications in the medical field. In particular Van Broekhoven (US 4,956,581 and US 4,952,382) has described their use in SO_x abatement chemistry.

15 SUMMARY OF THE INVENTION

This invention relates to a new process for the preparation of anionic clay and boehmite-containing compositions. Optionally, these compositions may also contain unreacted trivalent metal source and/or divalent metal source.

20 The process according to the invention comprises reacting a divalent metal source with aluminium trihydrate or a thermally treated form thereof and optionally another trivalent metal source in aqueous suspension in one or more steps. During the reaction, boehmite is formed from aluminium trihydrate or its thermally treated form. Because this aluminium source is less expensive than
25 boehmite, the process offers a cheaper way of producing anionic clay and boehmite-containing compositions than prior art methods.

Another advantage of the invention is that the anionic clay to boehmite ratio can easily be controlled. This can be especially useful for catalysis or adsorption
30 purposes. Anionic clay mainly possesses basic sites; boehmite primarily consists of acidic sites. Therefore, by varying the anionic clay to boehmite ratio,

the ratio of acidic to basic sites can be changed.

Moreover, by varying the reaction conditions the ratio micro-crystalline boehmite to quasi-crystalline boehmite in the composition can be tuned. For instance, under hydrothermal conditions mainly micro-crystalline boehmite is formed, whereas at lower temperatures quasi-crystalline boehmite is the main constituent.

To obtain a catalyst composition comprising an anionic clay and boehmite-containing composition obtainable by the process according to the invention, the anionic clay and boehmite-containing composition is added to a slurry containing the other catalyst components or precursors thereof and finally shaped.

DETAILED DESCRIPTION OF THE INVENTION

Our invention relates to a process for the preparation of anionic clay and boehmite-containing compositions. This process involves the use of inexpensive starting materials, such as oxides, hydroxides, carbonates, and hydroxy carbonates. Therefore, washing and filtering steps are not essential in this process. Moreover, this process is particularly environmental-friendly and more suited to the environmental constraints which are increasingly imposed on commercial operations.

The process comprises the reaction of a divalent metal source and aluminium trihydrate or a thermally treated form thereof and optionally another trivalent metal source. Boehmite is formed from aluminium trihydrate or its thermally treated form. The resulting compositions may also contain unreacted (which means: not reacted to anionic clay or boehmite) divalent metal compounds, aluminium trihydrate and/or other trivalent metal compounds.

Boehmite is present in the resulting composition. In this specification, boehmite

must be regarded as any type of boehmite, like micro-crystalline boehmite (MCB), quasi-crystalline boehmite (QCB) and mixtures thereof.

QCB aluminas usually have very high surface areas, large pores and high pore volumes. They have lower specific densities and contain larger amounts of intercalated water molecules upon hydration than MCBs (about 1.4-2.0 moles of water per mole of Al for QCBs and about 1.0-1.4 moles of water per mole of Al for MCBs). Moreover, QCBs differ from MCBs by having larger amounts of crystal imperfections and smaller crystal sizes. Therefore, QCBs show much broader peaks in their Powder X-ray diffraction (PXRD) patterns than MCBs. The half-widths of QCBs typically vary from about 2 to 6 degrees 2-theta (2θ). Further, as the amount of water intercalated into the QCB crystal increases, the main (020) XRD reflection moves to lower 2θ values, corresponding to greater d-spacings.

For the purpose of this specification we define quasi-crystalline boehmites to have 020 peak widths at half-length of the maximum intensity of at least 1.5 degrees 2θ . Boehmites having a 020 peak width at half-length of the maximum intensity smaller than 1.5 degrees 2θ are considered micro-crystalline boehmites.

20 Aluminium trihydrate

In the present invention aluminium trihydrate includes crystalline aluminium trihydrate (ATH), for example gibbsite provided by Reynolds Aluminium Company RH-20® or JM Huber Micral® grades. Also BOC (Bauxite Ore Concentrate), bayerite and nordstrandite are suitable aluminium trihydrates. BOC is the cheapest alumina source. The alumina trihydrate is preferred to have a particle size ranging from 1 to 150 μm , more preferably smaller than 20 μm . In another embodiment of the invention thermally treated forms of gibbsite are used. Combinations of aluminium trihydrate and thermally treated forms of aluminium trihydrate can also be used. The calcined aluminium trihydrate is readily obtained by thermally treating aluminium trihydrate (gibbsite) at a

temperature above 100°C, preferably ranging from 100° to 800°C for 15 minutes to 24 hours. In any event, the calcining temperature and time for obtaining calcined aluminium trihydrate should be sufficient to cause a measurable increase of the surface area compared to the surface area of the gibbsite as produced by the Bayer process which is generally between 30 and 50 m²/g. It should be noted that within the context of this invention flash calcined alumina is also considered to be a thermally treated form of aluminium trihydrate, although generally it is considered a very specific alumina. Flash calcined alumina is obtained by treating aluminium trihydrate at temperatures between 800°-1000°C for very short periods of time in special industrial equipment, as is described in US 4,051,072 and US 3,222,129. Combinations of various thermally treated forms of aluminium trihydrate can also be used. Preferably the aluminium trihydrate or its thermally treated form is added to the reactor in the form of a slurry. In particular we emphasise that there is no need to use a peptisable alumina source (gibbsite is not peptisable) and as a result no need to add either mineral or organic acid to vary the pH of the mixture. In the process according to our invention other aluminium sources beside aluminium trihydrate or its thermally treated forms may be added to the aqueous suspension such as oxides and hydroxides of aluminium (e.g. sols, flash calcined alumina, gels, quasi-crystalline boehmite, micro-crystalline boehmite), aluminium salts such as aluminium nitrate, aluminium chloride, aluminium chlorohydrate and sodium aluminate. Said other aluminium sources may be soluble or insoluble in water and may be added to the aluminium trihydrate and/or its thermally treated form or it may be added to the aqueous suspension separately as a solid, a solution or as a suspension.

Aluminium trihydrate or its thermally treated form may be doped with metal compounds like for instance rare earth metals or transition metals. Examples include compounds of B, Ce, La, V, Zn, Cu, Co and combinations thereof. The dopants can be present in amounts between 1 and 50 wt%, preferably lower than 25 wt% and more preferably lower than 10 wt%. This doped aluminium

trihydrate (or its thermally treated form) can be obtained by thermal or hydrothermal treatment of aluminium trihydrate with the dopant. Preferably oxides, hydroxides and carbonates of the above-indicated metals are used, but also nitrates, chlorides, sulphates and phosphates can be used. When this
5 doped aluminium trihydrate (or its thermally treated form) is used as a starting material for the compositions according to the invention, doped boehmite will be present in the final product. This may be beneficial for several applications.

Other trivalent metal sources

10 The other trivalent metal sources that can be used for preparing the anionic clay and boehmite-containing composition can be salts, hydroxides, oxides or alkoxides of trivalent metals such as B, Ga, In, Bi, Fe, Cr, Sc, La, Ce, and mixtures of these compounds. Preferably oxides, hydroxides, carbonates, hydroxy carbonates, carboxylates or alkoxides are used. Both solid trivalent
15 metal sources and soluble trivalent metal sources are suitable. Combinations of metal sources may be used as well. The metal source may be fed to the reactor as a solid, a solution, or, preferably, as a slurry.

Divalent metal source

20 Suitable divalent metal sources to be used in the process according to the invention are compounds containing Mg^{2+} , Ca^{2+} , Ba^{2+} , the transition metals Zn^{2+} , Mn^{2+} , Co^{2+} , Mo^{2+} , Ni^{2+} , Fe^{2+} , Sr^{2+} , Cu^{2+} , and mixtures of said compounds. Preferably oxides, hydroxides, carbonates or hydroxy carbonates are used. Both solid divalent metal sources and soluble divalent metal sources are
25 suitable. Combinations of metal sources may be used as well. The metal source may be fed to the reactor as a solid, a solution, or, preferably, as a slurry. The metal source may also be combined with the trivalent metal source before it is fed to the reactor. Especially when using metal sources like oxides, hydroxides, carbonates or hydroxy carbonates, it is usually advisable to mill the
30 metal source before use. Preferably, both the trivalent metal source and the divalent metal source are milled before use. When wet milling is used, the slurry

containing both the trivalent metal source and the divalent metal source may be wet milled, for instance in a ball mill.

Conditions

- 5 A divalent metal source, aluminium trihydrate or a thermally treated form thereof, and optionally another trivalent metal source are added to a reactor and reacted in aqueous suspension to obtain the anionic clay and boehmite-containing composition. Within the context of this invention a reactor is considered to be any confined zone in which the reaction between the trivalent
- 10 metal source and the divalent metal source takes place. The reactor may be equipped with stirrers, baffles etcetera to ensure homogeneous mixing of the reactants. The reaction can take place with or without stirring, at ambient or at elevated temperature and at atmospheric or elevated pressure. Usually, a temperature between 0° and 100°C is used at or above atmospheric pressure.
- 15 It is preferred to carry out the process at temperatures above 50°C rather than at room temperature, because this results in compositions with sharper peaks in the X-ray diffraction pattern than anionic clay and boehmite-containing compositions obtained at room temperature. The reactor may be heated by any heating source such as a furnace, microwave, infrared sources, heating jackets
- 20 (either electrical or with a heating fluid), lamps, etcetera. Because of its simplicity, this process is particularly suitable to be carried out in a continuous mode.
- Said aqueous suspension in the reactor may be obtained by either adding
- 25 slurries of the starting materials, either combined or separate, to the reactor or adding the divalent metal source to a slurry of aluminium trihydrate and optionally another trivalent metal source or vice versa and adding the resulting slurry to the reactor. It is possible to treat, for instance, the slurry containing aluminium trihydrate at elevated temperature and then add either the divalent
- 30 metal source and the optional other trivalent metal source per se, or add the these metal sources in a slurry or solution either to the reactor or the aluminium

trihydrate slurry. The solids to liquid ratio in the reactor is preferably less than 40 wt%, and ranges more preferably from 10 to 20 wt%.

5 The divalent metal to trivalent metal molar ratio used in the process according to the invention is less than 3, preferably less than 2 and most preferably less than 1. By varying this ratio the anionic clay to boehmite ratio in the final product can be tuned. The desired ratio will depend on the application of the final product.

10 If the only trivalent metal source used in the process is aluminium trihydrate or a thermally treated form thereof, it is added in such an amount that beside anionic clay also boehmite is formed.

15 If a combination of aluminium trihydrate (or its thermally treated form) and another trivalent metal is used, these compounds have to be added in such amounts that beside anionic clay also boehmite is formed. These amounts will depend on the nature of the other trivalent metal and its reactivity towards anionic clay formation. The exact amounts can easily be obtained by routine experimentation.

20 The process can be conducted hydrothermally. Within the context of this description hydrothermal means in the presence of water (or steam) at a temperature above 100°C at increased pressure, e.g. autogenous pressure. This hydrothermal treatment is particularly advantageous, because this is faster and a higher conversion is obtained. There is no need to wash or filter the product, as unwanted ions (e.g. sodium, chloride, sulphate, phosphate) which
25 are frequently encountered when using prior art preparation methods, are absent in the product.

30 In a further embodiment of the invention, the process is conducted in a multiple step fashion, e.g. a slurry of divalent metal source, aluminium trihydrate (or its thermally treated form) and optionally another trivalent metal source is treated hydrothermally in a first reactor, followed by thermal treatment at milder

conditions in a second reactor or vice versa. In between these two steps either the amount of aluminium trihydrate (or its thermally treated form) needed to form the boehmite in the final composition, or additional amounts of aluminium trihydrate (or its thermally treated form) can be added. Especially the latter
5 embodiment offers a good way to vary the MCB/QCB ratio, because under hydrothermal conditions mainly MCB is formed, whereas at lower temperatures (i.e. lower than 85°C) substantially QCB is formed.

If desired, organic or inorganic acids and bases, for example for control of the
10 pH, may be fed to the reactor or added to either one of the metal sources before they are fed to the reactor. The pH may vary over a wide range and may depend on the MCB/QCB ratio that is desired. At low pH more QCB will be formed, at high pH more MCB will be formed. An example of a preferred pH modifier is an ammonium base, because upon drying no deleterious cations remain in the
15 anionic clay.

The resulting composition may optionally be calcined at temperatures between 300° and 1200°C, preferably 300° to 800°C and most preferably 300°-600°C for 15 minutes to 24 hours, preferably 1-12 hours and most preferably 2-6 hours.
20 By this treatment the anionic clay will be transformed into a solid solution and/or spinel. Solid solutions possess the well known memory effect, which means that they can be transformed back into anionic clays upon rehydration. This rehydration can be performed by contacting the solid solution-containing composition in water for 1-24 hours at 65°-85°C. Preferably, the slurry is stirred
25 and has a solids content ranging from about 10 to 50 wt%. During this treatment additives can be added.

The present invention is therefore also directed to a process wherein an anionic clay and boehmite-containing composition prepared by the process according to the composition is heat-treated at a temperature between 300° and 1200°C
30 to form a solid solution and/or spinel-containing composition, optionally followed to an anionic clay-containing composition.

If desired, the anionic clay and boehmite-containing composition prepared by the process according to the invention may be subjected to ion-exchange. Upon ion-exchange the interlayer charge-balancing anions are replaced with
5 other anions. Examples of suitable anions are carbonates, bicarbonates, nitrates, chlorides, sulphates, bisulphates, vanadates, tungstates, borates, phosphates, and pillaring anions such as $V_2O_7^{4-}$, $HV_2O_{12}^{4-}$, $V_3O_9^{3-}$, $V_{10}O_{28}^{6-}$, $Mo_7O_{24}^{6-}$, $PW_{12}O_{40}^{3-}$, $B(OH)_4^-$, $B_4O_5(OH)_4^{2-}$, $[B_3O_3(OH)_4]^-$, $[B_3O_3(OH)_5]^{2-}$, HBO_4^{2-} , $HGaO_3^{2-}$, CrO_4^{2-} , Keggin-ions, formates, acetate and mixtures thereof. Said ion-
10 exchange can be conducted before or after drying the anionic clay and boehmite-containing composition formed in the slurry.

For some applications it is desirable to have additives, both metal compounds and non-metal compounds, comprising rare earth metals, Si, P, B, group VI,
15 group VIII, alkaline earth (for instance Ca and Ba) and/or transition metals (for example Mn, Fe, Ti, Zr, Cu, Ni, Zn, Mo, V, W, Sn), present. Said additives can easily be deposited on the anionic clay and boehmite-containing composition according to the invention or they can be added either to the divalent metal source or trivalent metal source which are added to the reactor or added to the
20 reactor separately. Suitable sources of metal compounds or non-metal compounds are oxides, halides or any other salt such as chlorides, nitrates etcetera. In the case of a multi-step process the additives may be added in any of the steps. This can be especially advantageous for controlling the distribution of the additives in the anionic clay.

25

The resulting compositions can advantageously be used as adsorbent, catalyst additive or matrix. Boehmite, already present in the composition, acts as a binder for the anionic clay in the composition. These compositions are very suitable for sulphur and nitrogen reduction in gasoline and diesel fuels and for
30 SO_x/NO_x removal in FCC units. By varying the individual components in the composition the effectiveness of the adsorbent can be optimised.

The compositions prepared by the process according to the invention are also suitable as metal trap in the FCC unit. The compositions are especially advantageous for this purpose due to the control of the MCB/QCB ratio within the composition. For example, QCBs are known to convert heavier bottoms to lighter products, whereas MCBs are effective agents to passivate nickel and vanadium metal contaminants. Therefore, the compositions according to the invention, wherein the ratio of the different types of boehmite can be controlled, are very useful in catalysts for the conversion of heavy bottoms.

10

Catalyst compositions comprising anionic clay and boehmite-containing compositions are prepared by

- a. preparing an anionic clay and boehmite-containing composition obtainable by the process according to the invention,
- 15 b. adding the composition to a slurry containing the other catalyst components or precursors thereof, and
- c. shaping the resulting composition

The anionic clay and boehmite-containing composition can be added to the slurry of step b in suspended form or as a dry powder (dried for instance between 100° and 200°C). Optionally, acid or base treatment, thermal or hydrothermal treatment or a combination thereof is performed on the anionic clay and boehmite-containing composition before addition to the slurry. The slurry may contain conventional catalyst components such as matrix or filler materials (e.g. clay, such as kaolin, titanium oxide, zirconia, alumina, silica, silica-alumina, bentonite, etcetera) and/or molecular sieve material (e.g. ZSM-5, zeolite Y, etcetera). The slurry is preferably kept at a temperature in the range 15° to 40°C and standard pressure for a time ranging from 1 minute to 4 hours.

30 The resulting catalyst compositions are shaped. Suitable shaping methods include spray-drying, pelletising, extrusion (optionally combined with kneading),

- beading, or any other conventional shaping method used in the catalyst and absorbent fields or combinations thereof. The amount of liquid present in the slurry used for shaping should be adapted to the specific shaping step to be conducted. It might be advisable to partially remove the liquid used in the slurry and/or add an additional or another liquid, and/or change the pH of the precursor mixture to make the slurry gellable and thus suitable for shaping. Various additives commonly used in the various shaping methods such as extrusion additives may be added to the precursor mixture used for shaping.
- 5
- 10 The resulting catalyst compositions comprise 5 to 40 wt% of the anionic clay and boehmite-containing composition.

The present invention is illustrated by the following examples.

15 EXAMPLES

Comparative Example A

- This Comparative Example illustrates a standard way to prepare anionic clay from aluminium trihydrate and MgO, without excess aluminium trihydrate.
- 20

- A mixture of 3.92 g MgO and 2.5 g gibbsite (Alcoa CP®) was slurried in 50 ml of de-ionised water. The slurry was treated at 65°C for 14 hours. The Mg/Al ratio was approximately 2.3. The product was dried at 90°C overnight. Powder X-ray diffraction (PXRD) showed the presence of anionic clay and no boehmite.
- 25

Example 1

- A mixture of 3.92 g MgO and 1.88 g gibbsite (Alcoa CP®) was slurried in 50 ml of de-ionised water. The slurry was treated at 65°C overnight. The Mg/Al ratio was approximately 3. The product was dried at 90°C overnight. PXRD showed
- 30

the presence of anionic clay and no boehmite.

This product (3.68 g) was slurried with 8.59 g of gibbsite (Alcoa CP®). The suspension was hydrothermally treated at 185°C for 4 hours. The product was dried at 95°C overnight. PXRD showed the presence of anionic clay and boehmite.

5

Example 2

46.5 g aluminium trihydrate was slurried in 466 g de-ionised water containing 389.6 g $\text{Fe}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The final slurry contained 13 wt% solids. The total amount of slurry was 976 g. The slurry was homogenised and reacted for 5 hours at 65°C, followed by a hydrothermal treatment at 175°C for 2 hours. The product was dried at 110°C overnight. PXRD showed the formation of an anionic clay along with boehmite.

15

Example 3

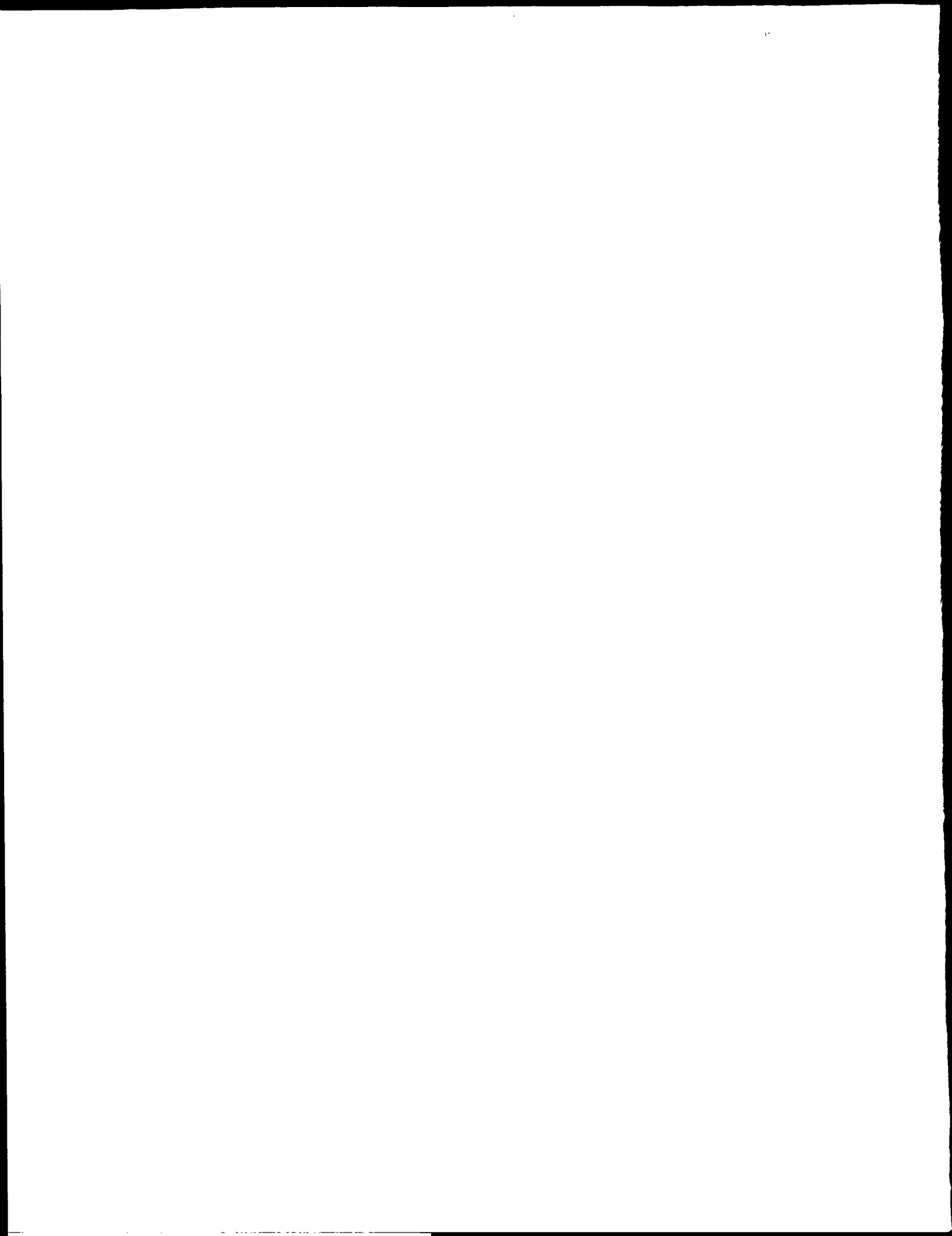
A mixture of 3.92 g MgO and 11.30 g gibbsite (Alcoa CP®) was slurried in 70 ml de-ionised water and treated at 65°C for 14 hours. The Mg/Al ratio was approximately 0.5. The product was dried at 90°C overnight. PXRD indicated the presence of anionic clay along with a significant amount of pseudo-boehmite and brucite.

20

Example 4

The product of Example 3 (10 g) was slurried in 40 ml de-ionised water, placed in an Anton Parr hydrothermal apparatus and treated at 185°C for 4 hours. During this treatment, the slurry was stirred. A significant narrowing of the boehmite reflections in the PXRD pattern indicated the conversion of pseudo-boehmite into a more crystalline form.

30



EPO - DG 1

05. 03. 2001

16

ACH 2852 PDEP

(38)

CLAIMS:

- 5 1. Process for the preparation of an anionic clay and boehmite-containing composition, characterised in that the process comprises reacting a divalent metal source, aluminium trihydrate or a thermally treated form thereof and optionally another trivalent metal source in a one step or multiple step fashion to obtain a composition comprising anionic clay and boehmite.
- 10 2. Process according to claim 1, characterised in that reaction is conducted in a one step fashion.
- 15 3. Process according to claim 2, characterised in that the reaction is performed under hydrothermal conditions.
- 20 4. Process according to claim 1, characterised in that reaction is conducted in a two step fashion.
5. Process according to claim 4, characterised in that the reaction in the first step is conducted under hydrothermal conditions and in the second step under non-hydrothermal conditions.
- 25 6. Process according to claim 4 or 5, characterised in that in between the two steps additional aluminium trihydrate or a thermally treated form thereof is added to the reactor.
7. Process according to any one of the previous claims, characterised in that the process is conducted in a continuous mode.
- 30 8. Process according to any one of the previous claims, characterised in that the divalent metal compound is an oxide, hydroxide, carbonate of hydroxy

carbonate of magnesium or a transition metal.

9. Process according to claim 8, characterised in that the transition metal is copper or zinc.
- 5 10. Process according to any one of the previous claims, characterised in that metal compounds or non-metal compounds are fed to the reactor or deposited on the final composition.
- 10 11. Process according to any one of the previous claims, characterised in that the anionic clay is subjected to an ion-exchange treatment.
- 15 12. Process for the preparation of a solid solution and/or spinel-containing composition, wherein an anionic clay and boehmite-containing composition obtained by any one of the processes of any one of the previous claims is subjected to a heat-treatment at a temperature between 3000 and 1200 °C.
- 20 13. Process for the preparation of an anionic clay-containing composition, characterised in that the solid solution-containing composition obtained by the process of claim 12 is rehydrated to form an anionic clay-containing composition.
14. Anionic clay and boehmite-containing composition obtainable by the process according to any one of the previous claims.
- 25 15. Catalyst composition comprising an anionic clay and boehmite-containing composition according to claim 14.
16. Process for the preparation of a catalyst composition according to claim 15, comprising the steps of
- 30 a. preparing a composition according to claim 14,
b. adding the composition to a slurry containing the other catalyst

18

ACH 2852 PDEP

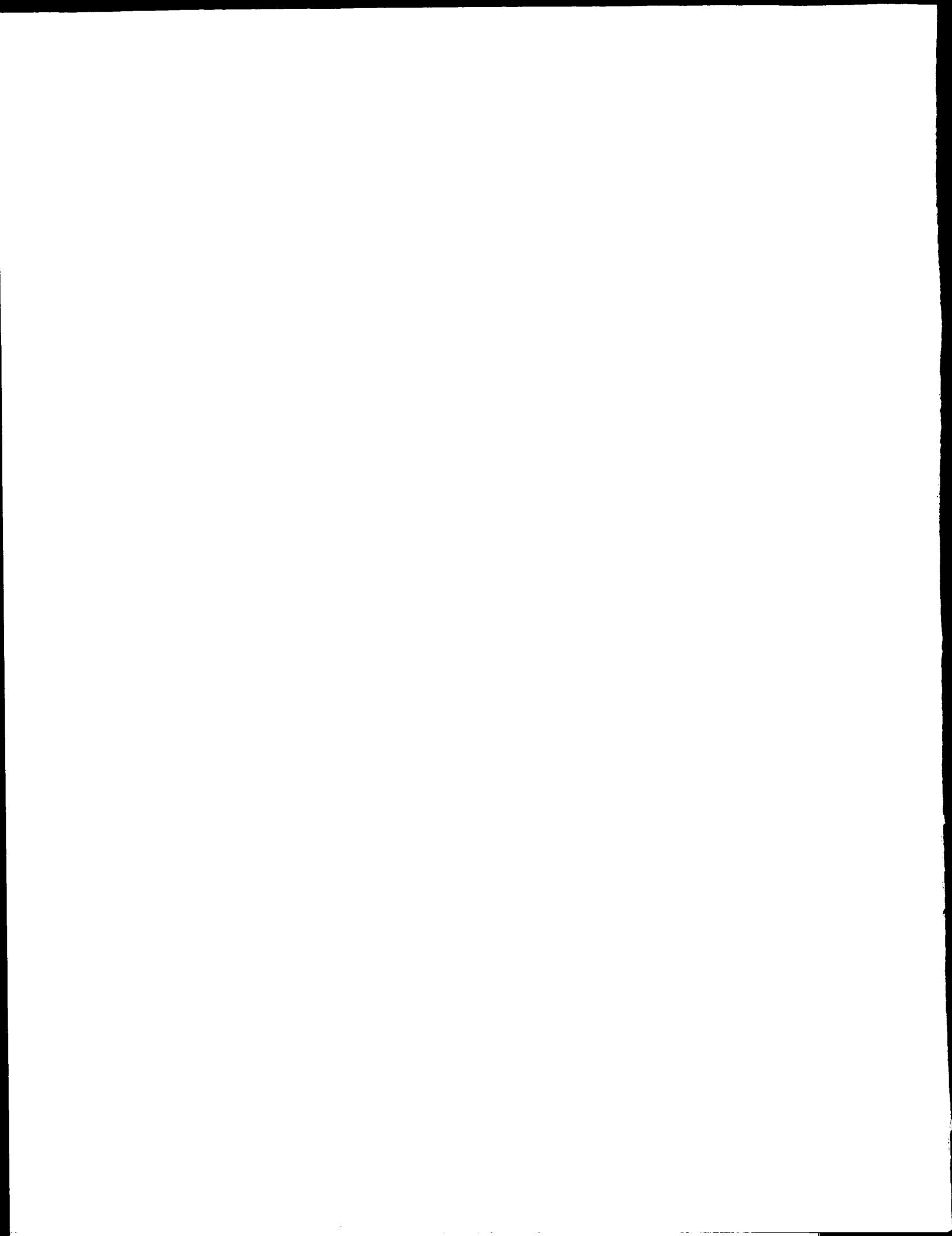
- components or precursors thereof, and
- c. shaping the resulting composition.

17. Process according to claim 16, characterised in that the composition
5 according to claim 14 is treated with an acid or base before adding to the
slurry of step b.

18. Process according to claim 16 or 17, characterised in that the composition
10 according to claim 14 is treated thermally or hydrothermally before adding to
the slurry of step b.

19. Process according to any one of the claims 16-18, characterised in that the
composition according claim 14 is added to the slurry of step b in
15 suspended form.

20. Process according to any one of the claims 16-18, characterised in that the
composition according claim 14 is added to the slurry of step b in a dry form.



EPO - DG 1

05. 03. 2001

19

ACH 2852 PDEP

ABSTRACT

(38)

This invention relates to a new process for the preparation of anionic clay and boehmite-containing compositions. These compositions may also contain
5 unreacted trivalent metal source and/or divalent metal source. The process according to the invention comprises reacting a divalent metal source, aluminium trihydrate or a thermally treated form thereof and optionally another trivalent metal source in a one step or multiple step fashion to obtain a composition comprising anionic clay and boehmite. During the reaction,
10 boehmite is formed from aluminium trihydrate or its thermally treated form.

This process offers a cheaper way of producing anionic clay and boehmite-containing compositions than prior art methods. Another advantage of the invention is that the anionic clay to boehmite ratio, and therefore ratio of acidic to basic sites can be controlled. Moreover, by varying the reaction conditions
15 the ratio micro-crystalline boehmite to quasi-crystalline boehmite in the composition can be tuned.

